

Figure 2.2 Reductive dehalogenation of chlorinated ethenes.

the accumulation of daughter products and an increase in the concentration of chloride ions. Reductive dechlorination affects each of the chlorinated ethenes differently. Of these compounds, PCE is the most susceptible to reductive dechlorination because it is the most oxidized. Conversely, VC is the least susceptible to reductive dechlorination because it is the least oxidized of these compounds. As a result, the rate of reductive dechlorination decreases as the degree of chlorination decreases (Vogel and McCarty, 1985; Bouwer, 1994). Murray and Richardson (1993) have postulated that this rate decrease may explain the accumulation of VC in PCE and TCE plumes that are undergoing reductive dechlorination. Reductive dechlorination has been demonstrated under nitrate- and iron-reducing conditions, but the most rapid biodegradation rates, affecting the widest range of chlorinated aliphatic hydrocarbons, occur under sulfate-reducing and methanogenic conditions (Bouwer, 1994). Because chlorinated aliphatic hydrocarbon compounds are used as electron acceptors during reductive dechlorination, there must be an appropriate source of carbon for microbial growth in order for this process to occur (Bouwer, 1994). Potential carbon sources include natural organic matter, fuel hydrocarbons, or other anthropogenic organic compounds such as those found in landfill leachate.

2.2.1.1.2 *Electron Donor Reactions*

Murray and Richardson (1993) write that microorganisms are generally believed to be incapable of growth using PCE and TCE as a primary substrate (i.e., electron donor). However, under aerobic and some anaerobic conditions, the less oxidized chlorinated aliphatic hydrocarbons (e.g., VC) can be used as the primary substrate in biologically mediated oxidation-reduction reactions (McCarty and Semprini, 1994). In this type of reaction, the facilitating microorganism obtains energy and organic carbon from the degraded chlorinated aliphatic hydrocarbon. In contrast to reactions in which the chlorinated aliphatic hydrocarbon is used as an electron acceptor, only the least oxidized chlorinated aliphatic hydrocarbons can be used as electron donors in biologically mediated oxidation-reduction reactions. McCarty and Semprini (1994) describe investigations in which VC and 1,2-dichloroethane (DCA) were shown to serve as primary substrates under aerobic conditions. These authors also document that dichloromethane has the potential to function as a primary substrate under either aerobic or anaerobic environments. In addition, Bradley and Chapelle (1996) show evidence of mineralization of VC under iron-reducing conditions so long as there is sufficient bioavailable iron (III). Aerobic metabolism of VC may be characterized by a loss of VC mass and a decreasing molar ratio of VC to other chlorinated aliphatic hydrocarbon compounds. In addition, Klier *et al.* (1998) and Bradley and Chapelle (1997) show mineralization of DCE to carbon dioxide under aerobic, Fe(III) reducing, and methanogenic conditions, respectively.

2.2.1.1.3 *Cometabolism*

When a chlorinated aliphatic hydrocarbon is biodegraded via cometabolism, the degradation is catalyzed by an enzyme or cofactor that is fortuitously produced by the organisms for other purposes. The organism receives no known benefit from the degradation of the chlorinated aliphatic hydrocarbon. Rather, the cometabolic degradation of the chlorinated aliphatic hydrocarbon may in fact be harmful to the microorganism responsible for the production of the enzyme or cofactor (McCarty and Semprini, 1994). Cometabolism is best documented in aerobic environments, although it potentially could occur under anaerobic conditions. It has been reported that under aerobic conditions chlorinated ethenes, with the exception of PCE, are susceptible to cometabolic degradation (Murray and Richardson, 1993; Vogel, 1994; McCarty and Semprini, 1994). Vogel (1994) further elaborates that the rate of cometabolism increases as the degree of dechlorination decreases. During cometabolism, the chlorinated alkene is indirectly transformed by bacteria as they use BTEX or

another substrate to meet their energy requirements. Therefore, the chlorinated alkene does not enhance the degradation of BTEX or other carbon sources, nor will its cometabolism interfere with the use of electron acceptors involved in the oxidation of those carbon sources.

2.2.1.2 Behavior of Chlorinated Solvent Plumes

Chlorinated solvent plumes can exhibit three types of behavior depending on the amount of solvent, the amount of biologically available organic carbon in the aquifer, the distribution and concentration of natural electron acceptors, and the types of electron acceptors being used. Individual plumes may exhibit all three types of behavior in different portions of the plume. The different types of plume behavior are summarized below.

2.2.1.2.1 Type 1 Behavior

Type 1 behavior occurs where the primary substrate is anthropogenic carbon (e.g., BTEX or landfill leachate), and microbial degradation of this anthropogenic carbon drives reductive dechlorination. When evaluating natural attenuation of a plume exhibiting Type 1 behavior, the following questions must be answered:

- 1) Is the electron donor supply adequate to allow microbial reduction of the chlorinated organic compounds? In other words, will the microorganisms “strangle” before they “starve” (i.e., will they run out of chlorinated aliphatic hydrocarbons used as electron acceptors before they run out of anthropogenic carbon used as the primary substrate)?
- 2) What is the role of competing electron acceptors (e.g., dissolved oxygen, nitrate, iron (III) and sulfate)?
- 3) Is VC oxidized, or is it reduced?

Appendices B and C discuss what these questions mean and how they are answered. Type 1 behavior results in the rapid and extensive degradation of the more highly-chlorinated solvents such as PCE, TCE, and DCE.

2.2.1.2.2 Type 2 Behavior

Type 2 behavior dominates in areas that are characterized by relatively high concentrations of biologically available native organic carbon. Microbial utilization of this natural carbon source drives reductive dechlorination (i.e., it is the primary substrate for microorganism growth). When evaluating natural attenuation of a Type 2 chlorinated solvent plume, the same questions as those posed in the description of Type 1 behavior must be answered. Type 2 behavior generally results in slower biodegradation of the highly chlorinated solvents than Type 1 behavior, but under the right conditions (e.g., areas with high natural organic carbon contents), this type of behavior also can result in rapid degradation of these compounds.

2.2.1.2.3 Type 3 Behavior

Type 3 behavior dominates in areas that are characterized by inadequate concentrations of native and/or anthropogenic carbon, and concentrations of dissolved oxygen that are greater than 1.0 mg/L. Under these aerobic conditions, reductive dechlorination will not occur. The most significant natural attenuation mechanisms for PCE, TCE, and DCE will be advection, dispersion, and sorption. However, VC can be rapidly oxidized under these conditions. Type 3 behavior also occurs in ground water that does not contain microbes capable of biodegradation of chlorinated solvents.

2.2.1.2.4 Mixed Behavior

As mentioned above, a single chlorinated solvent plume can exhibit all three types of behavior in different portions of the plume. This can be beneficial for natural biodegradation of chlorinated aliphatic hydrocarbon plumes. For example, Wiedemeier *et al.* (1996a) describe a plume at Plattsburgh AFB, New York, that exhibits Type 1 behavior in the source area and Type 3 behavior downgradient from the source. The most fortuitous scenario involves a plume in which PCE, TCE, and DCE are reductively dechlorinated with accumulation of VC near the source area (Type 1 or Type 2 behavior), then VC is oxidized (Type 3 behavior), either aerobically or via iron reduction further downgradient. Vinyl chloride is oxidized to carbon dioxide in this type of plume and does not accumulate. The following sequence of reactions occurs in a plume that exhibits this type of mixed behavior.



In general, TCE, DCE, and VC may attenuate at approximately the same rate, and thus these reactions may be confused with simple dilution. Note that no ethene is produced during this reaction. Vinyl chloride is removed from the system much faster under these conditions than it is under VC-reducing conditions.

A less desirable scenario, but one in which all contaminants may be entirely biodegraded, involves a plume in which all chlorinated aliphatic hydrocarbons are reductively dechlorinated via Type 1 or Type 2 behavior. Vinyl chloride is reduced to ethene, which may be further reduced to ethane or methane. The following sequence of reactions occurs in this type of plume.



This sequence has been investigated by Freedman and Gossett (1989). In this type of plume, VC degrades more slowly than TCE, and thus tends to accumulate.

2.2.2 Bioattenuation Screening Process

An accurate assessment of the potential for natural biodegradation of chlorinated compounds should be made before investing in a detailed study of natural attenuation. The screening process presented in this section is outlined in Figure 2.3. This approach should allow the investigator to determine if natural bioattenuation of PCE, TCE, DCE, TCA, and chlorobenzenes is likely to be a viable remedial alternative before additional time and money are expended. If the site is regulated under CERCLA, much of the data required to make the preliminary assessment of natural attenuation will be used to evaluate alternative engineered remedial solutions as required by the NCP. Table 2.3 presents the analytical screening criteria.

For most of the chlorinated solvents, the initial biotransformation in the environment is a reductive dechlorination. The initial screening process is designed to recognize geochemical environments where reductive dechlorination is plausible. It is recognized, however, that bioodegradation of certain halogenated compounds can also proceed via oxidative pathways. Examples include DCE, VC, the dichloroethanes, chloroethane, dichlorobenzenes, monochlorobenzene, methylene chloride, and ethylene dibromide.

The following information is required for the screening process:

- The chemical and geochemical data presented in Table 2.3 for background and target areas of the plume as depicted in Figure 2.4. Figure 2.4 shows the schematic locations of these data collection points. Note: If other contaminants are suspected, then data on the concentrations and distribution of these compounds also should be obtained.
- Locations of source(s) and potential points of exposure. If subsurface NAPLs are sources, estimate extent of residual and free-phase NAPL.
- An estimate of the transport velocity and direction of ground-water flow.

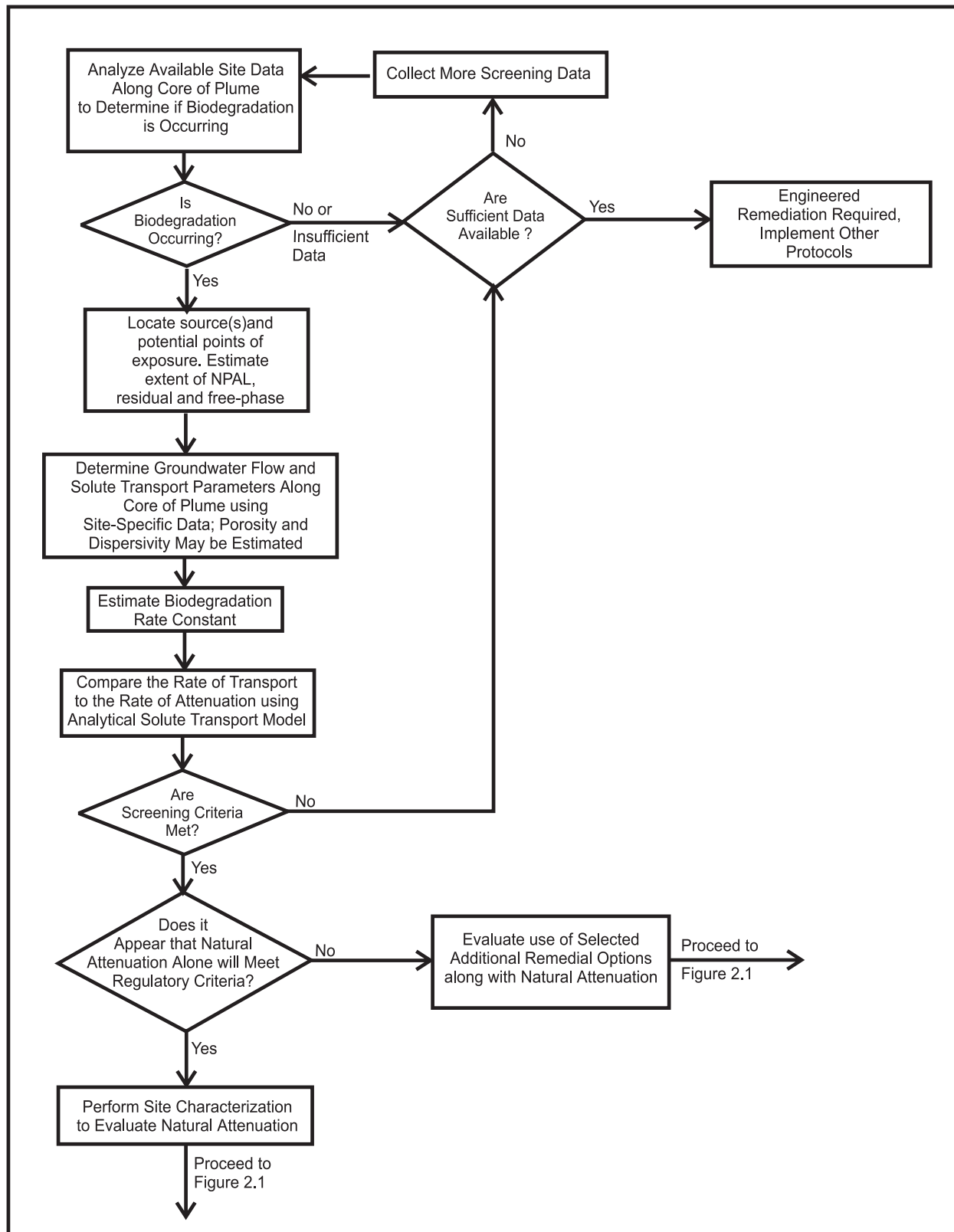


Figure 2.3 Initial screening process flow chart.

Table 2.3 Analytical Parameters and Weighting for Preliminary Screening for Anaerobic Biodegradation Processes^{a/}

Analysis	Concentration in Most Contaminated Zone	Interpretation	Value
Oxygen*	<0.5 mg/L	Tolerated, suppresses the reductive pathway at higher concentrations	3
Oxygen*	>5 mg/L	Not tolerated; however, VC may be oxidized aerobically	-3
Nitrate*	<1 mg/L	At higher concentrations may compete with reductive pathway	2
Iron II*	>1 mg/L	Reductive pathway possible; VC may be oxidized under Fe(III)-reducing conditions	3
Sulfate*	<20 mg/L	At higher concentrations may compete with reductive pathway	2
Sulfide*	>1 mg/L	Reductive pathway possible	3
Methane*	<0.5 mg/L	VC oxidizes	0
	>0.5 mg/L	Ultimate reductive daughter product, VC Accumulates	3
Oxidation Reduction Potential* (ORP) against Ag/AgCl electrode	<50 millivolts (mV) <-100mV	Reductive pathway possible	1
		Reductive pathway likely	2
pH*	5 < pH < 9	Optimal range for reductive pathway	0
	5 > pH >9	Outside optimal range for reductive pathway	-2
TOC	> 20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature*	> 20°C	At T >20°C biochemical process is accelerated	1
Carbon Dioxide	>2x background	Ultimate oxidative daughter product	1
Alkalinity	>2x background	Results from interaction between CO ₂ and aquifer minerals	1
Chloride*	>2x background	Daughter product of organic chlorine	2
Hydrogen	>1 nM	Reductive pathway possible, VC may accumulate	3
Hydrogen	<1 nM	VC oxidized	0
Volatile Fatty Acids	> 0.1 mg/L	Intermediates resulting from biodegradation of more complex compounds; carbon and energy source	2
BTEX*	> 0.1 mg/L	Carbon and energy source; drives dechlorination	2
Tetrachloroethene		Material released	0
Trichloroethene*		Material released	0
		Daughter product of PCE	2 ^{a/}
DCE*		Material released	0
		Daughter product of TCE	2 ^{a/}
		If cis is > 80% of total DCE it is likely a daughter product 1,1-DCE can be chemical reaction product of TCA	
VC*		Material released	0
		Daughter product of DCE	2 ^{a/}
1,1,1-Trichloroethane*		Material released	0
DCA		Daughter product of TCA under reducing conditions	2
Carbon Tetrachloride		Material released	0
Chloroethane*		Daughter product of DCA or VC under reducing conditions	2
Ethene/Ethane	>0.01mg/L	Daughter product of VC/ethene	2
	>0.1 mg/L		3
Chloroform		Material released	0
		Daughter product of Carbon Tetrachloride	2
Dichloromethane		Material released	0
		Daughter product of Chloroform	2

* Required analysis. a/ Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).

Once these data have been collected, the screening process can be undertaken. The following steps summarize the screening processes:

- 1) Determine if biodegradation is occurring using geochemical data. If biodegradation is occurring, proceed to step 2. If it is not, assess the amount and types of data available. If data are insufficient to determine if biodegradation is occurring, collect supplemental data. If all the recommended screening parameters listed in section 2.2 have been collected and the screening processes suggest that natural attenuation is not appropriate, the screening processes are finished. Perform site characterization to evaluate other remediation alternatives.
- 2) Determine ground-water flow and solute transport parameters from representative field data. Dispersivity and porosity may be estimated from literature but the hydraulic conductivity and the ground-water gradient and flow direction must be determined from field data. The investigator should use the highest valid hydraulic conductivity measured at the site during the preliminary screening because solute plumes tend to follow the path of least resistance (i.e., highest hydraulic conductivity). This will give the “worst-case” estimate of the solute migration distance over a given period of time. Compare this “worst-case” estimate with the rate of plume migration determined from site characterization data. Determine what degree of plume migration is acceptable or unacceptable with respect to site-specific remediation objectives.
- 3) Locate source(s) and potential points of exposure. If subsurface NAPLs are sources, estimate extent of residual and free-phase NAPL.
- 4) Estimate the biodegradation rate constant. Biodegradation rate constants can be estimated using a conservative tracer found commingled with the contaminant plume, as described in Appendix C and by Wiedemeier *et al.* (1996b). When dealing with a plume that contains chlorinated solvents, this procedure can be modified to use chloride as a tracer. Rate constants derived from microcosm studies can also be used when site specific field data are inadequate or inconclusive. If it is not possible to estimate the biodegradation rate using these procedures, then use a range of accepted literature values for biodegradation of the contaminants of concern. Appendix C presents a range of biodegradation rate constants for various compounds. Although literature values may be used to estimate biodegradation rates in the bioattenuation screening process described in Section 2.2, literature values should not be used in the later more detailed analysis of natural attenuation, described in Section 2.3.
- 5) Compare the rate of transport to the rate of attenuation.
Use analytical solutions or a screening model such as BIOSCREEN.
- 6) Determine if screening criteria are met.

Step 1: Determine if Biodegradation is Occurring

The first step in the screening process is to sample or use existing data for the areas represented in Figure 2.4 and analyze them for the parameters listed in Table 2.3 (see also Section 2.3.2). These areas should include (1) the most contaminated portion of the aquifer (generally in the “source” area with NAPL or high concentrations of contaminants in ground water ; (2) downgradient from the source area but still in the dissolved contaminant plume; (3) downgradient from the dissolved contaminant plume; and (4) upgradient and lateral locations that are not impacted by the plume. Although this figure is a simplified two-dimensional representation of the features of a contaminant plume, real plumes are three-dimensional objects. The sampling should be conducted in accordance with Appendix A.

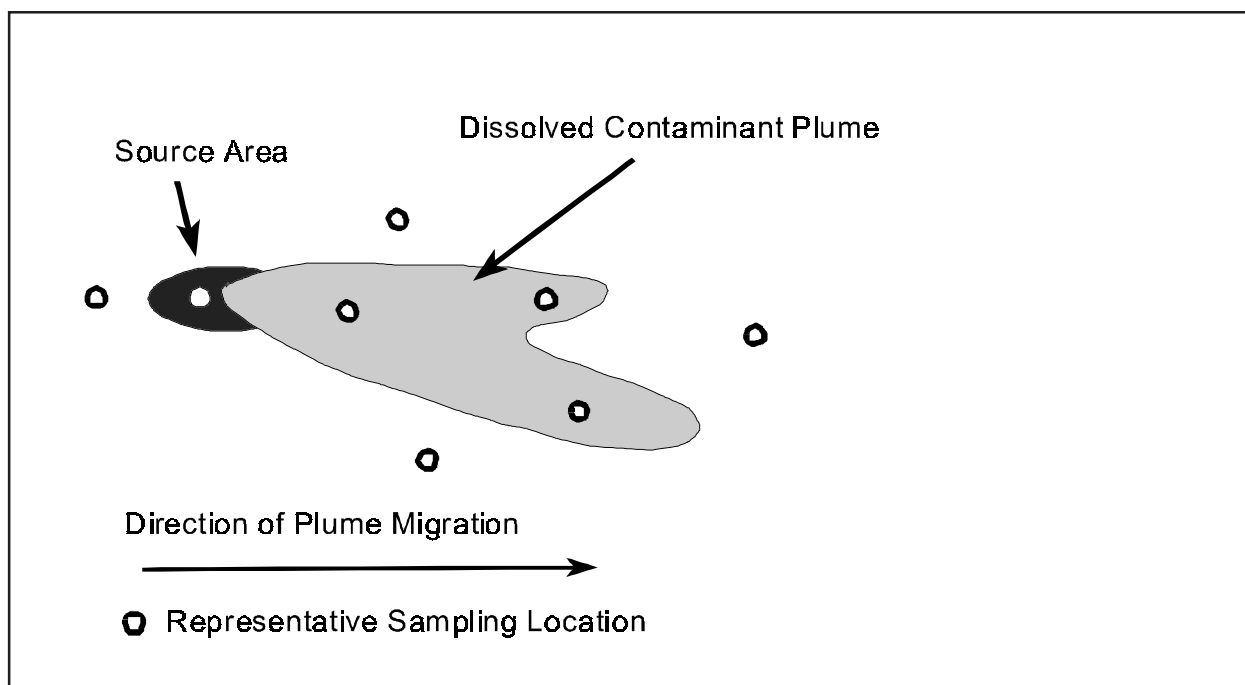


Figure 2.4 Target areas for collecting screening data. Note that the number and location of monitoring wells will vary with the three dimensional complexity of the plume(s).

The sample collected in the NAPL source area provides information as to the predominant terminal electron-accepting process at the source area. In conjunction with the sample collected in the NAPL source zone, samples collected in the dissolved plume downgradient from the NAPL source zone allow the investigator (1) to determine if the plume is degrading with distance along the flow path and (2) to determine the distribution of electron acceptors and donors and metabolic by-products along the flow path. The sample collected downgradient from the dissolved plume aids in plume delineation and allows the investigator to determine if metabolic byproducts are present in an area of ground water that has been remediated. The upgradient and lateral samples allow delineation of the plume and determination of background concentrations of the electron acceptors and donors.

After these samples have been analyzed for the parameters listed in Table 2.3, the investigator should analyze the data to determine if biodegradation is occurring. The right-hand column of Table 2.3 contains scoring values that can be used as a test to assess the likelihood that biodegradation is occurring. This method relies on the fact that biodegradation will cause predictable changes in ground water chemistry. For example, if the dissolved oxygen concentration in the area of the plume with the highest contaminant concentration is less than 0.5 milligrams per liter (mg/L), 3 points are awarded. Table 2.4 summarizes the range of possible scores and gives an interpretation for each score. If the score totals 15 or more points, it is likely that biodegradation is occurring, and the investigator should proceed to Step 2.

Table 2.4 Interpretation of Points Awarded During Screening Step 1

Score	Interpretation
0 to 5	Inadequate evidence for anaerobic biodegradation* of chlorinated organics
6 to 14	Limited evidence for anaerobic biodegradation* of chlorinated organics
15 to 20	Adequate evidence for anaerobic biodegradation* of chlorinated organics
> 20	Strong evidence for anaerobic biodegradation* of chlorinated organics
*reductive dechlorination	

The following two examples illustrate how Step 1 of the screening process is implemented. The site used in the first example is a former fire training area contaminated with chlorinated solvents mixed with fuel hydrocarbons. The presence of the fuel hydrocarbons appears to reduce the ORP of the ground water to the extent that reductive dechlorination is favorable. The second example contains data from a dry cleaning site contaminated only with chlorinated solvents. This site was contaminated with spent cleaning solvents that were dumped into a shallow dry well situated just above a well-oxygenated, unconfined aquifer with low organic carbon concentrations of dissolved organic carbon.

Example 1: Strong Evidence for Anaerobic Biodegradation (Reductive Dechlorination) of Chlorinated Organics

Analyte	Concentration in Most Contaminated Zone	Points Awarded
Dissolved Oxygen	0.1 mg/L	3
Nitrate	0.3 mg/L	2
Iron (II)	10 mg/L	3
Sulfate	2 mg/L	2
Methane	5 mg/L	3
ORP	-190 mV	2
Chloride	3 times background	2
PCE (released)	1,000 µg/L	0
TCE (none released)	1,200 µg/L	2
cis-DCE (none released)	500 µg/L	2
VC (none released)	50 µg/L	2
Total Points Awarded		23 Points

In this example, the investigator can infer that biodegradation is likely occurring at the time of sampling and may proceed to Step 2.

Example 2: Anaerobic Biodegradation (Reductive Dechlorination) Unlikely

Analyte	Concentration in Most Contaminated Zone	Points Awarded
Dissolved Oxygen	3 mg/L	-3
Nitrate	0.3 mg/L	2
Iron (II)	Not Detected (ND)	0
Sulfate	10 mg/L	2
Methane	ND	0
ORP	+ 100 mV	0
Chloride	background	0
TCE (released)	1,200 µg/L	0
cis-DCE (none released)	ND	0
VC (none released)	ND	0
Total Points Awarded		1 Point

In this example, the investigator can infer that biodegradation is probably not occurring or is occurring too slowly to contribute to natural attenuation at the time of the sampling. In this case, the investigator should evaluate whether other natural attenuation processes can meet the cleanup objectives for the site (e.g., abiotic degradation or transformation, volatilization or sorption) or select a remedial option other than MNA.

Step 2: Determine Ground-water Flow and Solute Transport Parameters

After it has been shown that biodegradation is occurring, it is important to quantify ground-water flow and solute transport parameters. This will make it possible to use a solute transport model to quantitatively estimate the concentration of the plume and its direction and rate of travel. To use an analytical model, it is necessary to know the hydraulic gradient and hydraulic conductivity for the site and to have estimates of porosity and dispersivity. It also is helpful to know the coefficient of retardation. Quantification of these parameters is discussed in detail in Appendix B.

In order to make the modeling as accurate as possible, the investigator must have site-specific hydraulic gradient and hydraulic conductivity data. To determine the ground-water flow and solute transport direction, it is necessary to have at least three accurately surveyed wells in each hydrogeologic unit of interest at the site. The porosity and dispersivity are generally estimated using accepted literature values for the aquifer matrix materials containing the plume at the site. If the investigator has total organic carbon data for soil, it is possible to estimate the coefficient of retardation; otherwise, it is conservative to assume that the solute transport and ground-water velocities are the same. Techniques to collect these data are discussed in the appendices.

Step 3: Locate Sources and Receptor Exposure Points

To determine the length of flow for the predictive modeling to be conducted in Step 5, it is important to know the distance between the source of contamination, the leading edge along the core of the dissolved plume, and any potential downgradient or cross-gradient receptor exposure points.

Step 4: Estimate the Biodegradation Rate

Biodegradation is the most important process that degrades contaminants in the subsurface; therefore, the biodegradation rate is one of the most important model input parameters. Biodegradation of chlorinated aliphatic hydrocarbons can be represented as a first-order rate constant. Whenever possible, use site-specific biodegradation rates estimated from field data collected along the core of the plume. Calculation of site-specific biodegradation rates is discussed in Appendix C. If it is not possible to determine site-specific biodegradation rates, then literature values may be used in a sensitivity analysis (Table C.3.5). A useful approach is to start with average values, and then to vary the model input to predict “best-case” and “worst-case” scenarios. Estimated biodegradation rates can be used only after it has been shown that biodegradation is occurring (see Step 1). Although literature values may be used to estimate biodegradation rates in the bioattenuation screening process described in Section 2.2, additional site information should be collected to determine biodegradation rates for the site when refining the site conceptual model, as described in Section 2.3. Literature values should not be used during the more detailed analysis.

Step 5: Compare the Rate of Transport to the Rate of Attenuation

At this early stage in the natural attenuation demonstration, comparison of the rate of solute transport to the rate of attenuation is best accomplished using an analytical model. Several models are available. It is suggested that the decay option be first order for use in any of the models.

The primary purpose of comparing the rate of transport to the rate of natural attenuation is to determine if natural attenuation processes will be capable of attaining site-specific remediation objectives in a time period that is reasonable compared to other alternatives (i.e., to quantitatively

estimate if site contaminants are attenuating at a rate fast enough to prevent further plume migration and restore the plume to appropriate cleanup levels). The analytical model BIOSCREEN can be used to determine whether natural attenuation processes will be capable of meeting site-specific remediation objectives at some distance downgradient of a source. The numerical model BIOPLUME III can be used to estimate whether site contaminants are attenuating at a rate fast enough to restore the plume to appropriate cleanup levels. It is important to perform a sensitivity analysis to help evaluate the confidence in the preliminary screening modeling effort. For the purposes of the screening effort, if modeling shows that the screening criteria are met, the investigator can proceed with the natural attenuation evaluation.

Step 6: Determine if Screening Criteria are Met

Before proceeding with the full-scale natural attenuation evaluation, the investigator should ensure that the answers to both of the following questions are “yes”:

- Has the plume moved a shorter distance than would be expected based on the known (or estimated) time since the contaminant release and the contaminant velocity in ground water, as calculated from site-specific measurements of hydraulic conductivity and hydraulic gradient, and estimates of effective porosity and contaminant retardation?
- Is it likely that site contaminants are attenuating at rates sufficient to meet remediation objectives for the site in a time period that is reasonable compared to other alternatives?

If the answers to these questions are “yes,” then the investigator is encouraged to proceed with the full-scale natural attenuation demonstration.

2.3 COLLECT ADDITIONAL SITE CHARACTERIZATION DATA TO EVALUATE NATURAL ATTENUATION AS REQUIRED

It is the responsibility of the proponent to “make the case” for natural attenuation. Thus, a credible and thorough site assessment is necessary to document the potential for natural attenuation to meet cleanup objectives. As discussed in Section 2.1, review of existing site characterization data is particularly useful before initiating site characterization activities. Such review should allow identification of data gaps and guide the most effective placement of additional data collection points.

There are two goals during the site characterization phase of a natural attenuation investigation. The first is to collect the data needed to determine if natural mechanisms of contaminant attenuation are occurring at rates sufficient to attain site-specific remediation objectives in a time period that is reasonable compared to other alternatives. The second is to provide sufficient site-specific data to allow prediction of the future extent and concentrations of a contaminant plume through solute fate and transport modeling. Thus, detailed site characterization is required to achieve these goals and to support this remedial option. Adequate site characterization in support of natural attenuation requires that the following site-specific parameters be determined:

- Location, nature, and extent of contaminant source area(s) (i.e., areas containing mobile or residual NAPL or highly contaminated ground water).
- Chemical properties (e.g., composition, solubility, volatility, etc.) of contaminant source materials.
- The potential for a continuing source due to sewers, leaking tanks, or pipelines, or other site activity.
- Extent and types of soil and ground-water contamination.
- Aquifer geochemical parameters (Table 2.1).

- Regional hydrogeology, including:
 - Drinking water aquifers, and
 - Regional confining units.
- Local and site-specific hydrogeology, including:
 - Local drinking water aquifers;
 - Location of industrial, agricultural, and domestic water wells;
 - Patterns of aquifer use (current and future);
 - Lithology;
 - Site stratigraphy, including identification of transmissive and nontransmissive units;
 - Potential pathways for NAPL migration (e.g., surface topography and dip of confining layers);
 - Grain-size distribution (sand vs. silt vs. clay);
 - Aquifer hydraulic conductivity;
 - Ground water hydraulic information;
 - Preferential flow paths;
 - Locations and types of surface water bodies; and
 - Areas of local ground water recharge and discharge.
- Identification of current and future potential exposure pathways, receptors, and exposure points.

Many chlorinated solvent plumes have enough three-dimensional expression to make it impossible for a single well to adequately describe the plume at a particular location on a map of the site.

Figure 2.5 depicts a cross section of a hypothetical site with three-dimensional expression of the plume. A documented source exists in the capillary fringe just above the water table. Such sources are usually found by recovering, extracting, and analyzing core material. This material can be (1) a release of LNAPL containing chlorinated solvents; (2) a release of pure chlorinated solvents that has been entrapped by capillary interactions in the capillary fringe; or (3) material that has experienced high concentrations of solvents in solution in ground water, has sorbed the solvents, and now is slowly desorbing the chlorinated solvents. Recharge of precipitation through this source produces a plume that appears to dive into the aquifer as it moves away from the source. This effect can be caused by recharge of clean ground water above the plume as it moves downgradient of the source, by collection of the plume into more hydraulically conductive material at the bottom of the aquifer, or by density differences between the plume and the unimpacted ground water.

Below the first hydrologic unit there is a second unit that has fine-textured material at the top and coarse-textured material at the bottom of the unit. In the hypothetical site, the fine-textured material at the top of the second unit has inhibited downward migration of a DNAPL, causing it to spread laterally at the bottom of the first unit and form a second source of ground-water contamination in the first unit. Because DNAPL below the water table tends to exist as diffuse and widely extended ganglia rather than of pools filling all the pore space, it is statistically improbable that the material sampled by conventional core sampling will contain DNAPL. Because these sources are so difficult to sample, these sources are cryptic to conventional sampling techniques.

At the hypothetical site, DNAPL has found a pathway past the fine-textured material and has formed a second cryptic source area at the bottom of the second hydrologic unit. Compare Figure 2.6. The second hydrologic unit at the hypothetical site has a different hydraulic gradient than the first unit. As a result, the plume in the second unit is moving in a different direction than the plume in the first unit. Biological processes occurring in one hydrologic unit may not occur in another; a plume may show Type 2 behavior in one unit and Type 3 behavior in another.

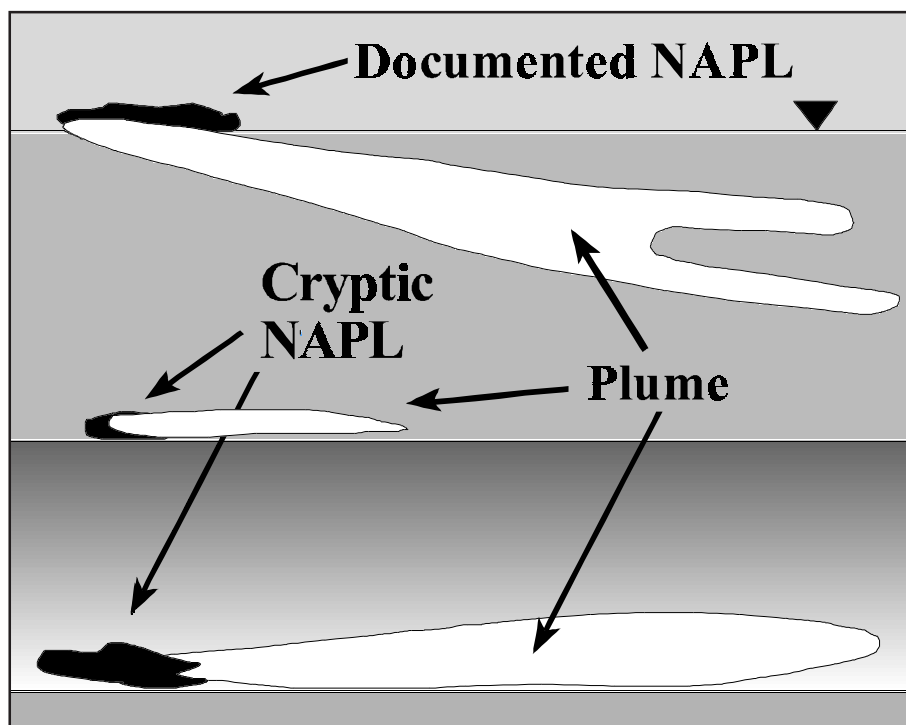


Figure 2.5 A cross section through a hypothetical release, illustrating the three-dimensional character of the plumes that may develop from a release of chlorinated solvents.

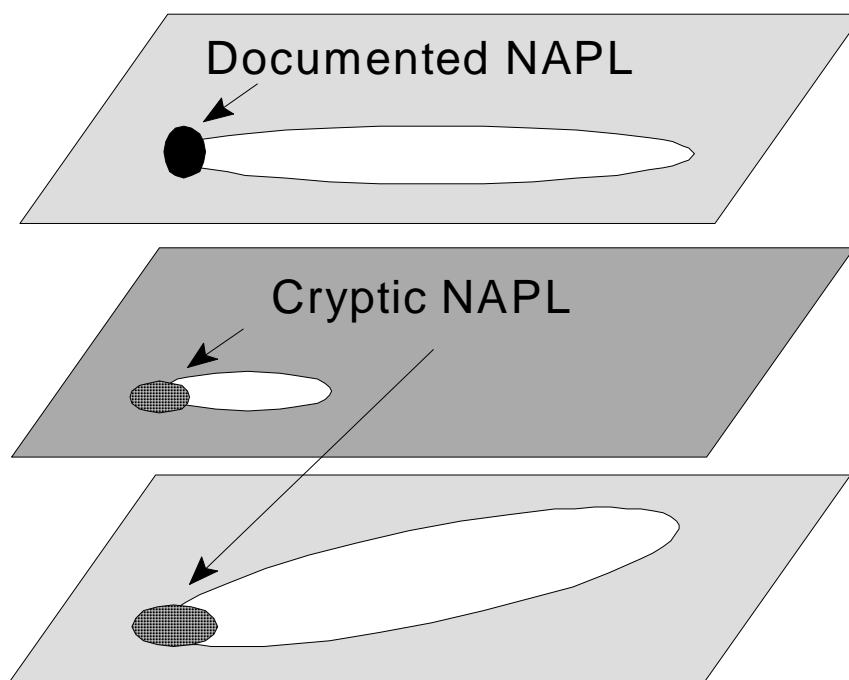


Figure 2.6 A stacked plan representation of the plumes that may develop from the hypothetical release depicted in Figure 2.5. Each plan representation depicts a separate plume that can originate from discrete source areas produced from the same release of chlorinated solvents.

As a consequence, it is critical to sample and evaluate the three-dimensional character of the site with respect to (1) interaction of contaminant releases with the aquifer matrix material, (2) local hydrological features that control development and migration of plumes, and (3) the geochemical interactions that favor bioattenuation of chlorinated solvents.

The following sections describe the methodologies that should be implemented to allow successful site characterization in support of natural attenuation.

2.3.1 Characterization of Soils and Aquifer Matrix Materials

In order to adequately define the subsurface hydrogeologic system and to determine the three-dimensional distribution of mobile and residual NAPL that can act as a continuing source of ground-water contamination, credible and thorough soil characterization must be completed. As appropriate, soil gas data may be collected and analyzed to better characterize soil contamination in the vadose zone. Depending on the status of the site, this work may have been completed during previous remedial investigation work. The results of soils characterization will be used as input into a solute fate and transport model to help define a contaminant source term and to support the natural attenuation investigation.

The purpose of sampling soil and aquifer matrix material is to determine the subsurface distribution of hydrostratigraphic units and the distribution of mobile and residual NAPL, as well as pore water that contains high concentrations of the contaminants in the dissolved phase. These objectives can be achieved through the use of conventional soil borings or direct-push methods (e.g., Geoprobe® or cone penetrometer testing), and through collection of soil gas samples. All samples should be collected, described, analyzed, and disposed of in accordance with local, State, and Federal guidance. Appendix A contains suggested procedures for sample collection. These procedures may require modification to comply with local, State, and Federal regulations or to accommodate site-specific conditions.

The analytical methods to be used for soil, aquifer matrix material, and soil gas sample analyses is presented in Table 2.1. This table includes all of the parameters necessary to document natural attenuation, including the effects of sorption, volatilization, and biodegradation. Each analyte is discussed separately below.

- **Volatile Organic Compounds:** Knowledge of the location, distribution, concentration, and total mass of contaminants sorbed to soils or present as mobile or immobile NAPL is required to calculate contaminant partitioning from NAPL into ground water. This information is useful to predict the long-term persistence of source areas. Knowledge of the diffusive flux of volatile organic compounds from NAPLs or ground water to the atmosphere or other identified receptor for vapors is required to estimate exposure of the human population or ecological receptors to contaminant vapors. If the flux of vapors can be compared to the discharge of the contaminants in ground water, the contribution of volatilization to natural attenuation of contamination in ground water can be documented.
- **Total Organic Carbon:** Knowledge of the TOC content of the aquifer matrix is important for sorption and solute-retardation calculations. TOC samples should be collected from a background location in the stratigraphic horizon(s) where most contaminant transport is expected to occur.
- **Oxygen and Carbon Dioxide:** Oxygen and carbon dioxide soil gas measurements can be used to identify areas in the unsaturated zone where biodegradation is occurring. This can be a useful and relatively inexpensive way to identify NAPL source areas, particularly when solvents are codisposed with fuels or greases (AFCEE, 1994).

- **Fuel and Chlorinated Volatile Organic Compounds:** Knowledge of the distribution of contaminants in soil gas can be used as a cost-effective way to estimate the extent of soil contamination.

2.3.2 Ground-water Characterization

To adequately determine the amount and three-dimensional distribution of dissolved contamination and to document the occurrence of natural attenuation, ground-water samples must be collected and analyzed. Biodegradation of organic compounds, whether natural or anthropogenic, brings about measurable changes in the chemistry of ground water in the affected area. By measuring these changes, it is possible to document and quantitatively evaluate the importance of natural attenuation at a site.

Ground-water sampling is conducted to determine the concentrations and distribution of contaminants, daughter products, and ground-water geochemical parameters. Ground-water samples may be obtained from monitoring wells or with point-source sampling devices such as a Geoprobe®, Hydropunch®, or cone penetrometer. All ground-water samples should be collected, handled, and disposed of in accordance with local, State, and Federal guidelines. Appendix A contains suggested procedures for ground-water sample collection. These procedures may need to be modified to comply with local, State, and Federal regulations or to accommodate site-specific conditions.

The analytical protocol for ground-water sample analysis is presented in Table 2.1. This analytical protocol includes all of the parameters necessary to delineate dissolved contamination and to document natural attenuation, including the effects of sorption and biodegradation. Data obtained from the analysis of ground water for these analytes is used to scientifically document natural attenuation and can be used as input into a solute fate and transport model. The following paragraphs describe each ground-water analytical parameter and the use of each analyte in the natural attenuation demonstration.

2.3.2.1 Volatile and Semivolatile Organic Compounds

These analytes are used to determine the type, concentration, and distribution of contaminants and daughter products in the aquifer. In many cases, chlorinated solvents are found commingled with fuels or other hydrocarbons. At a minimum, the volatile organic compound (VOC) analysis (Method SW8260A) should be used, with the addition of the trimethylbenzene isomers if fuel hydrocarbons are present or suspected. The combined dissolved concentrations of BTEX and trimethylbenzenes should not be greater than about 30 mg/L for a JP-4 spill (Smith *et al.*, 1981) or about 135 mg/L for a gasoline spill (Cline *et al.*, 1991; American Petroleum Institute, 1985). If these compounds are found in higher concentrations, sampling errors such as emulsification of LNAPL in the ground-water sample likely have occurred and should be investigated.

Maximum concentrations of chlorinated solvents dissolved in ground water from neat solvents should not exceed their solubilities in water. Appendix B contains solubilities for common contaminants. If contaminants are found in concentrations greater than their solubilities, then sampling errors such as emulsification of NAPL in the ground-water sample have likely occurred and should be investigated.

2.3.2.2 Dissolved Oxygen

Dissolved oxygen is the most thermodynamically favored electron acceptor used by microbes for the biodegradation of organic carbon, whether natural or anthropogenic. Anaerobic bacteria generally cannot function at dissolved oxygen concentrations greater than about 0.5 mg/L and, hence, reductive dechlorination will not occur. This is why it is important to have a source of carbon in the aquifer that can be used by aerobic microorganisms as a primary substrate. During

aerobic respiration, dissolved oxygen concentrations decrease. After depletion of dissolved oxygen, anaerobic microbes will use nitrate as an electron acceptor, followed by iron (III), then sulfate, and finally carbon dioxide (methanogenesis). Each sequential reaction drives the ORP of the ground water downward into the range within which reductive dechlorination can occur. Reductive dechlorination is most effective in the ORP range corresponding to sulfate reduction and methanogenesis, but dechlorination of PCE and TCE also may occur in the ORP range associated with denitrification or iron (III) reduction. Dehalogenation of DCE and VC generally are restricted to sulfate reducing and methanogenic conditions.

Dissolved oxygen measurements should be taken during well purging and immediately before and after sample acquisition using a direct-reading meter. Because most well purging techniques can allow aeration of collected ground-water samples, it is important to minimize the potential for aeration as described in Appendix A.

2.3.2.3 Nitrate

After dissolved oxygen has been depleted in the microbiological treatment zone, nitrate may be used as an electron acceptor for anaerobic biodegradation of organic carbon via denitrification. In order for reductive dechlorination to occur, nitrate concentrations in the contaminated portion of the aquifer must be less than 1.0 mg/L.

2.3.2.4 Iron (II)

In some cases, iron (III) is used as an electron acceptor during anaerobic biodegradation of organic carbon. During this process, iron (III) is reduced to iron (II), which may be soluble in water. Iron (II) concentrations can thus be used as an indicator of anaerobic degradation of fuel compounds, and vinyl chloride (see Section 2.2.1.1.2). Native organic matter may also support reduction of iron (II). Care must be taken when interpreting iron (II) concentrations because they may be biased low by reprecipitation as sulfides or carbonates.

2.3.2.5 Sulfate

After dissolved oxygen and nitrate have been depleted in the microbiological treatment zone, sulfate may be used as an electron acceptor for anaerobic biodegradation. This process is termed “sulfate reduction” and results in the production of sulfide. Concentrations of sulfate greater than 20 mg/L may cause competitive exclusion of dechlorination. However, in many plumes with high concentrations of sulfate, reductive dechlorination still occurs.

2.3.2.6 Methane

During methanogenesis acetate is split to form carbon dioxide and methane, or carbon dioxide is used as an electron acceptor, and is reduced to methane. Methanogenesis generally occurs after oxygen, nitrate, and sulfate have been depleted in the treatment zone. The presence of methane in ground water is indicative of strongly reducing conditions. Because methane is not present in fuel, the presence of methane above background concentrations in ground water in contact with fuels is indicative of microbial degradation of hydrocarbons. Methane also is associated with spills of pure chlorinated solvents (Weaver *et al.*, 1996). It is not known if the methane comes from chlorinated solvent carbon or from native dissolved organic carbon.

2.3.2.7 Alkalinity

There is a positive correlation between zones of microbial activity and increased alkalinity. Increases in alkalinity result from the dissolution of rock driven by the production of carbon dioxide produced by the metabolism of microorganisms. Alkalinity is important in the maintenance of ground-water pH because it buffers the ground water system against acids generated during both

aerobic and anaerobic biodegradation. In the experience of the authors, biodegradation of organic compounds rarely, if ever, generates enough acid to impact the pH of the ground water.

2.3.2.8 Oxidation-Reduction Potential

The ORP of ground water is a measure of electron activity and is an indicator of the relative tendency of a solution to accept or transfer electrons. Oxidation-reduction reactions in ground water containing organic compounds (natural or anthropogenic) are usually biologically mediated, and, therefore, the ORP of a ground water system depends upon and influences rates of biodegradation. Knowledge of the ORP of ground water also is important because some biological processes operate only within a prescribed range of ORP conditions.

ORP measurements can be used to provide real-time data on the location of the contaminant plume, especially in areas undergoing anaerobic biodegradation. Mapping the ORP of the ground water while in the field helps the field scientist to determine the approximate location of the contaminant plume. To map the ORP of the ground water while in the field, it is important to have at least one ORP measurement (preferably more) from a well located upgradient from the plume. ORP measurements should be taken during well purging and immediately before and after sample acquisition using a direct-reading meter. Because most well purging techniques can allow aeration of collected ground-water samples (which can affect ORP measurements), it is important to minimize potential aeration by using a flow-through cell as outlined in Appendix A.

Most discussion of oxidation reduction potential expresses the potential as if it were measured against the standard hydrogen electrode. Most electrodes and meters to measure oxidation-reduction potential use the silver/silver chloride electrode (Ag/AgCl) as the reference electrode. This protocol uses the potential against the Ag/AgCl electrode as the screening potential, not Eh as would be measured against the standard hydrogen electrode.

2.3.2.9 Dissolved Hydrogen

In some ground waters, PCE and TCE appear to attenuate, although significant concentrations of DCE and VC do not accumulate. In this situation, it is difficult to distinguish between Type 3 behavior where the daughter products are not produced, and Type 1 or Type 2 behavior where the daughter products are removed very rapidly. In cases like this, the concentration of hydrogen can be used to identify ground waters where reductive dechlorination is occurring. If hydrogen concentrations are very low, reductive dechlorination is not efficient and Type 3 behavior is indicated. If hydrogen concentrations are greater than approximately 1 nM, rates of reductive dechlorination should have environmental significance and Type 1 or Type 2 behavior would be expected.

Concentrations of dissolved hydrogen have been used to evaluate redox processes, and thus the efficiency of reductive dechlorination, in ground-water systems (Lovley and Goodwin, 1988; Lovley *et al.*, 1994; Chapelle *et al.*, 1995). Dissolved hydrogen is continuously produced in anoxic ground-water systems by fermentative microorganisms that decompose natural and anthropogenic organic matter. This H₂ is then consumed by respiratory microorganisms that use nitrate, Fe(III), sulfate, or CO₂ as terminal electron acceptors. This continuous cycling of H₂ is called *interspecies hydrogen transfer*. Significantly, nitrate-, Fe(III)-, sulfate- and CO₂-reducing (methanogenic) microorganisms exhibit different efficiencies in utilizing the H₂ that is being continually produced. Nitrate reducers are highly efficient H₂ utilizors and maintain very low steady-state H₂ concentrations. Fe(III) reducers are slightly less efficient and thus maintain somewhat higher H₂ concentrations. Sulfate reducers and methanogenic bacteria are progressively less efficient and maintain even higher H₂ concentrations. Because each terminal electron accepting process has a characteristic H₂ concentration associated with it, H₂ concentrations can be an indicator of predominant redox

processes. These characteristic ranges are given in Table 2.5. An analytical protocol for quantifying H_2 concentrations in ground water is given in Appendix A.

Table 2.5 Range of Hydrogen Concentrations for a Given Terminal Electron-Accepting Process

Terminal Electron Accepting Process	Hydrogen (H_2) Concentration (nanomoles per liter)
Denitrification	< 0.1
Iron (III) Reduction	0.2 to 0.8
Sulfate Reduction	1 to 4
Reductive Dechlorination	>1
Methanogenesis	5-20

Oxidation-reduction potential (ORP) measurements are based on the concept of thermodynamic equilibrium and, within the constraints of that assumption, can be used to evaluate redox processes in ground water systems. The H_2 method is based on the ecological concept of interspecies hydrogen transfer by microorganisms and, within the constraints of that assumption, can also be used to evaluate redox processes. These methods, therefore, are fundamentally different. A direct comparison of these methods (Chapelle et al., 1996) has shown that ORP measurements were effective in delineating oxic from anoxic ground water, but that ORP measurements could not distinguish between nitrate-reducing, Fe(III)-reducing, sulfate-reducing, or methanogenic zones in an aquifer. In contrast, the H_2 method could readily distinguish between different anaerobic zones. For those sites where distinguishing between different anaerobic processes is important, H_2 measurements are an available technology for making such distinctions. At sites where concentrations of redox sensitive parameters such as dissolved oxygen, iron (II), sulfide, and methane are sufficient to identify operative redox processes, H_2 concentrations are not always required to identify redox zonation and predict contaminant behavior.

In practice, it is preferable to interpret H_2 concentrations in the context of electron acceptor availability and the presence of the final products of microbial metabolism (Chapelle *et al.*, 1995). For example, if sulfate concentrations in ground water are less than 0.5 mg/L, methane concentrations are greater than 0.5 mg/L, and H_2 concentrations are in the 5 to 20 nM range, it can be concluded with a high degree of certainty that methanogenesis is the predominant redox process in the aquifer. Similar logic can be applied to identifying denitrification (presence of nitrate, H_2 < 0.1 nM), Fe(III) reduction (production of Fe(II), H_2 concentrations ranging from 0.2 to 0.8 nM), and sulfate reduction (presence of sulfate, production of sulfide, H_2 concentrations ranging from 1 to 4 nM). Reductive dechlorination in the field has been documented at hydrogen concentrations that support sulfate reduction or methanogenesis. If hydrogen concentrations are high enough to support sulfate reduction or methanogenesis, then reductive dechlorination is probably occurring, even if other geochemical indicators as scored in Table 2.3 do not indicate that reductive dechlorination is possible.

2.3.2.10 pH, Temperature, and Conductivity

Because the pH, temperature, and conductivity of a ground-water sample can change significantly within a short time following sample acquisition, these parameters must be measured in the field in unfiltered, unpreserved, “fresh” water collected by the same technique as the samples taken for dissolved oxygen and ORP analyses. The measurements should be made in a clean

container separate from those intended for laboratory analysis, and the measured values should be recorded in the ground-water sampling record.

The pH of ground water has an effect on the presence and activity of microbial populations in ground water. This is especially true for methanogens. Microbes capable of degrading chlorinated aliphatic hydrocarbons and petroleum hydrocarbon compounds generally prefer pH values varying from 6 to 8 standard units.

Ground-water temperature directly affects the solubility of dissolved gasses and other geochemical species. Ground-water temperature also affects the metabolic activity of bacteria.

Conductivity is a measure of the ability of a solution to conduct electricity. The conductivity of ground water is directly related to the concentration of ions in solution; conductivity increases as ion concentration increases.

2.3.2.11 Chloride

Chlorine is the most abundant of the halogens. Although chlorine can occur in oxidation states ranging from Cl^- to Cl^{+7} , the chloride form (Cl^-) is the only form of major significance in natural waters (Hem, 1985). Chloride forms ion pairs or complex ions with some of the cations present in natural waters, but these complexes are not strong enough to be of significance in the chemistry of fresh water (Hem, 1985). Chloride ions generally do not enter into oxidation-reduction reactions, form no important solute complexes with other ions unless the chloride concentration is extremely high, do not form salts of low solubility, are not significantly adsorbed on mineral surfaces, and play few vital biochemical roles (Hem, 1985). Thus, physical processes control the migration of chloride ions in the subsurface. Kaufman and Orlob (1956) conducted tracer experiments in ground water, and found that chloride moved through most of the soils tested more conservatively (i.e., with less retardation and loss) than any of the other tracers tested.

During biodegradation of chlorinated hydrocarbons dissolved in ground water, chloride is released into the ground water. This results in chloride concentrations in ground water in the contaminant plume that are elevated relative to background concentrations. Because of the neutral chemical behavior of chloride, it can be used as a conservative tracer to estimate biodegradation rates, as discussed in Appendix C.

2.3.3 Aquifer Parameter Estimation

Estimates of aquifer parameters are necessary to accurately evaluate contaminant fate and transport.

2.3.3.1 Hydraulic Conductivity

Hydraulic conductivity is a measure of an aquifer's ability to transmit water, and is perhaps the most important aquifer parameter governing fluid flow in the subsurface. The velocity of ground water and dissolved contamination is directly related to the hydraulic conductivity of the saturated zone. In addition, subsurface variations in hydraulic conductivity directly influence contaminant fate and transport by providing preferential paths for contaminant migration. Estimates of hydraulic conductivity are used to determine residence times for contaminants and tracers, and to determine the seepage velocity of ground water.

The most common methods used to quantify hydraulic conductivity are aquifer pumping tests and slug tests (Appendix A). Another method that may be used to determine hydraulic conductivity is the borehole dilution test. One drawback to these methods is that they average hydraulic properties over the screened interval. To help alleviate this potential problem, the screened interval of the test wells should be selected after consideration is given to subsurface stratigraphy.

Information about subsurface stratigraphy should come from geologic logs of continuous cores or from cone penetrometer tests. The rate of filling of a Hydropunch® can be used to obtain a rough estimate of the local hydraulic conductivity at the same time the water sample is collected. The results of pressure dissipation data from cone penetrometer tests can be used to supplement the results obtained from pumping tests and slug tests. It is important that the location of the aquifer tests be designed to collect information to delineate the range of hydraulic conductivity both vertically and horizontally at the site.

2.3.3.1.1 Pumping Tests in Wells

Pumping tests done in wells provide information on the average hydraulic conductivity of the screened interval, but not the most transmissive horizon included in the screened interval. In contaminated areas, the extracted ground water generally must be collected and treated, increasing the difficulty of such testing. In addition, a minimum 4-inch-diameter well is typically required to complete pumping tests in highly transmissive aquifers because the 2-inch submersible pumps available today are not capable of producing a flow rate high enough for meaningful pumping tests. In areas with fairly uniform aquifer materials, pumping tests can be completed in uncontaminated areas, and the results can be used to estimate hydraulic conductivity in the contaminated area. Pumping tests should be conducted in wells that are screened in the most transmissive zones in the aquifer. If pumping tests are conducted in wells with more than fifteen feet of screen, a down-hole flowmeter test can be used to determine the interval actually contributing to flow.

2.3.3.1.2 Slug Tests in Wells

Slug tests are a commonly used alternative to pumping tests. One commonly cited drawback to slug testing is that this method generally gives hydraulic conductivity information only for the area immediately surrounding the monitoring well. Slug tests do, however, have two distinct advantages over pumping tests: they can be conducted in 2-inch monitoring wells, and they produce no water. If slug tests are going to be relied upon to provide information on the three-dimensional distribution of hydraulic conductivity in an aquifer, multiple slug tests must be performed. It is not advisable to rely on data from one slug test in one monitoring well. Because of this, slug tests should be conducted at several zones across the site, including a test in at least two wells which are narrowly screened in the most transmissive zone. There should also be tests in the less transmissive zones to provide an estimate of the range of values present on the site.

2.3.3.1.3 Downhole Flowmeter

Borehole flowmeter tests are conducted to investigate the relative vertical distribution of horizontal hydraulic conductivity in the screened interval of a well or the uncased portion of a borehole. These tests can be done to identify any preferential flow pathways within the portion of an aquifer intersecting the test well screen or the open borehole. The work of Molz and Young (1993), Molz *et al.* (1994), Young and Pearson (1995), and Young (1995) describes the means by which these tests may be conducted and interpreted.

In general, measurements of ambient ground-water flow rates are collected at several regularly spaced locations along the screened interval of a well. Next, the well is pumped at a steady rate, and the measurements are repeated. The test data may be analyzed using the methods described by Molz and Young (1993) and Molz *et al.* (1994) to define the relative distribution of horizontal hydraulic conductivity within the screened interval of the test well. Estimates of bulk hydraulic conductivity from previous aquifer tests can be used to estimate the absolute hydraulic conductivity distribution at the test well.

Using flowmeter test data, one may be able to more thoroughly quantify the three-dimensional hydraulic conductivity distribution at a site. This is important for defining contaminant migration pathways and understanding solute transport at sites with heterogeneous aquifers. Even at sites where the hydrogeology appears relatively homogeneous, such data may point out previously undetected zones or layers of higher hydraulic conductivity that control contaminant migration. In addition, ground-water velocities calculated from hydraulic head, porosity, and hydraulic conductivity data may be used to evaluate site data or for simple transport calculations. In these cases, it is also important to have the best estimate possible of hydraulic conductivity for those units in which the contaminants are migrating.

2.3.3.2 Hydraulic Gradient

The horizontal hydraulic gradient is the change in hydraulic head (feet of water) divided by the distance of ground-water flow between head measurement points. To accurately determine the hydraulic gradient, it is necessary to measure ground-water levels in all monitoring wells and piezometers at a site. Because hydraulic gradients can change over a short distance within an aquifer, it is essential to have as much site-specific ground-water elevation information as possible so that accurate hydraulic gradient calculations can be made. In addition, seasonal variations in ground-water flow direction can have a profound influence on contaminant transport. Sites in upland areas are less likely to be affected by seasonal variations in ground-water flow direction than low-elevation sites situated near surface water bodies such as rivers and lakes.

To determine the effect of seasonal variations in ground-water flow direction on contaminant transport, quarterly ground-water level measurements should be taken over a period of at least one year. For many sites, these data may already exist. If hydraulic gradient data over a one-year period are not available, natural attenuation can still be implemented, pending an analysis of seasonal variation in ground-water flow direction.

2.3.3.3 Processes Causing an Apparent Reduction in Total Contaminant Mass

Several processes cause reductions in contaminant concentrations and apparent reductions in the total mass of contaminant in a system. Processes causing apparent reductions in contaminant mass include dilution, sorption, and hydrodynamic dispersion. In order to determine the mass of contaminant removed from the system, it is necessary to correct observed concentrations for the effects of these processes. This is done by incorporating independent assessments of these processes into the comprehensive solute transport model. The following sections give a brief overview of the processes that result in apparent contaminant reduction. Appendix B describes these processes in detail.

Dilution results in a reduction in contaminant concentrations and an apparent reduction in the total mass of contaminant in a system due to the introduction of additional water to the system. The two most common causes of dilution (real or apparent) are infiltration and sampling from monitoring wells screened over large vertical intervals. Infiltration can cause an apparent reduction in contaminant mass by mixing unaffected waters with the contaminant plume, thereby causing dilution. Monitoring wells screened over large vertical distances may dilute ground-water samples by mixing water from clean aquifer zones with contaminated water during sampling. To avoid potential dilution during sampling, monitoring wells should be screened over relatively small vertical intervals (e.g. 5 feet). Nested wells should be used to define the vertical extent of contamination in the saturated zone. Appendix C contains example calculations showing how to correct for the effects of dilution.

The retardation of organic solutes caused by sorption is an important consideration when simulating the effects of natural attenuation over time. Sorption of a contaminant to the aquifer matrix results in an apparent decrease in contaminant mass because dissolved contamination is removed from the aqueous phase. The processes of contaminant sorption and retardation are discussed in Appendix B.

The dispersion of organic solutes in an aquifer is another important consideration when simulating natural attenuation. The dispersion of a contaminant into relatively pristine portions of the aquifer allows the solute plume to mix with uncontaminated ground water containing higher concentrations of electron acceptors. Dispersion occurs vertically as well as parallel and perpendicular to the direction of ground-water flow.

To accurately determine the mass of contaminant transformed to innocuous by-products, it is important to correct measured contaminant concentrations for those processes that cause an apparent reduction in contaminant mass. This is accomplished by normalizing the measured concentration of each of the contaminants to the concentration of a tracer that is biologically recalcitrant. Because chloride is produced during the biodegradation of chlorinated solvents, this analyte can be used as a tracer. For chlorinated solvents undergoing reductive dechlorination, it is also possible to use the organic carbon in the original chlorinated solvent and daughter products as a tracer. Trimethylbenzene and tetramethylbenzene are two chemicals found in fuel hydrocarbon plumes that also may be useful as tracers. These compounds are difficult to biologically degrade under anaerobic conditions, and frequently persist in ground water longer than BTEX. Depending on the composition of the fuel that was released, other tracers may be used.

2.3.4 Optional Confirmation of Biological Activity

Extensive evidence can be found in the literature showing that biodegradation of chlorinated solvents and fuel hydrocarbons frequently occurs under natural conditions. Many references from the large body of literature in support of natural attenuation are listed in Section 3 and discussed in Appendix B. The most common technique used to show explicitly that microorganisms capable of degrading contaminants are present at a site is the microcosm study.

If additional evidence (beyond contaminant and geochemical data and supporting calculations) supporting natural attenuation is required, a microcosm study using site-specific aquifer materials and contaminants can be undertaken.

If properly designed, implemented, and interpreted, microcosm studies can provide very convincing documentation of the occurrence of biodegradation. Results of such studies are strongly influenced by the nature of the geological material submitted for study, the physical properties of the microcosm, the sampling strategy, and the duration of the study. Because microcosm studies are time-consuming and expensive, they should be undertaken only at sites where there is considerable uncertainty concerning the biodegradation of contaminants.

Biodegradation rate constants determined by microcosm studies often are higher than rates achieved in the field. The collection of material for the microcosm study, the procedures used to set up and analyze the microcosm, and the interpretation of the results of the microcosm study are presented in Appendix C.

2.4 REFINE CONCEPTUAL MODEL, COMPLETE PRE-MODELING CALCULATIONS, AND DOCUMENT INDICATORS OF NATURAL ATTENUATION

Site investigation data should first be used to refine the conceptual model and quantify ground-water flow, sorption, dilution, and biodegradation. The results of these calculations are used to scientifically document the occurrence and rates of natural attenuation and to help simulate natural

attenuation over time. It is the responsibility of the proponent to “make the case” for natural attenuation. This being the case, all available data must be integrated in such a way that the evidence is sufficient to support the conclusion that natural attenuation is occurring.

2.4.1 Conceptual Model Refinement

Conceptual model refinement involves integrating newly gathered site characterization data to refine the preliminary conceptual model that was developed on the basis of previously collected site-specific data. During conceptual model refinement, all available site-specific data should be integrated to develop an accurate three-dimensional representation of the hydrogeologic and contaminant transport system. This refined conceptual model can then be used for contaminant fate and transport modeling. Conceptual model refinement consists of several steps, including preparation of geologic logs, hydrogeologic sections, potentiometric surface/water table maps, contaminant and daughter product contour (isopleth) maps, and electron acceptor and metabolic by-product contour (isopleth) maps.

2.4.1.1 Geologic Logs

Geologic logs of all subsurface materials encountered during the soil boring phase of the field work should be constructed. Descriptions of the aquifer matrix should include relative density, color, major and minor minerals, porosity, relative moisture content, plasticity of fines, cohesiveness, grain size, structure or stratification, relative permeability, and any other significant observations such as visible contaminants or contaminant odor. It is also important to correlate the results of VOC screening using soil sample headspace vapor analysis with depth intervals of geologic materials. The depth of lithologic contacts and/or significant textural changes should be recorded to the nearest 0.1 foot. This resolution is necessary because preferential flow and contaminant transport paths may be limited to thin stratigraphic units.

2.4.1.2 Cone Penetrometer Logs

Cone Penetrometer Logs provide a valuable tool for the rapid collection of large amounts of stratigraphic information. When combined with the necessary corroborative physical soil samples from each stratigraphic unit occurring on the site, they can provide a three-dimensional model of subsurface stratigraphy.

Cone penetrometer logs express stratigraphic information as the ratio of sleeve friction to tip pressure. Cone penetrometer logs also may contain fluid resistivity data and estimates of aquifer hydraulic conductivity. To provide meaningful data, the cone penetrometer must be capable of providing stratigraphic resolution on the order of 3 inches. To provide accurate stratigraphic information, cone penetrometer logs must be correlated with continuous subsurface cores. At a minimum, there must be one correlation for every hydrostratigraphic unit found at the site. Cone penetrometer logs, along with geologic boring logs, can be used to complete the hydrogeologic sections discussed in Section 2.4.1.3.

2.4.1.3 Hydrogeologic Sections

Hydrogeologic sections should be prepared from boring logs and/or CPT data. A minimum of two hydrogeologic sections are required; one parallel to the direction of ground-water flow and one perpendicular to the direction of ground water flow. More complex sites may require more hydrogeologic sections. Hydraulic head data including potentiometric surface and/or water table elevation data should be plotted on the hydrogeologic section. These sections are useful in identifying potential pathways of contaminant migration, including preferential pathways of NAPL migration (e.g., surface topography and dip of confining layers) and of aqueous contaminants (e.g., highly

transmissive layers). The potential distribution NAPL sources as well as preferential pathways for solute transport should be considered when simulating contaminant transport using fate and transport models.

2.4.1.4 Potentiometric Surface or Water Table Map(s)

A potentiometric surface or water table map is a two-dimensional graphic representation of equipotential lines shown in plan view. These maps should be prepared from water level measurements and surveyor's data. Because ground water flows from areas of higher hydraulic head to areas of lower hydraulic head, such maps are used to estimate the probable direction of plume migration and to calculate hydraulic gradients. These maps should be prepared using water levels measured in wells screened in the same relative position within the same hydrogeologic unit. To determine vertical hydraulic gradients, separate potentiometric maps should be developed for different horizons in the aquifer to document vertical variations in ground-water flow. Flow nets should also be constructed to document vertical variations in ground-water flow. To document seasonal variations in ground-water flow, separate potentiometric surface or water table maps should be prepared for quarterly water level measurements taken over a period of at least one year. In areas with mobile LNAPL, a correction must be made for the water table deflection caused by accumulation of the LNAPL in the well. This correction and potentiometric surface map preparation are discussed in Appendix C.

2.4.1.5 Contaminant and Daughter Product Contour Maps

Contaminant and daughter product contour maps should be prepared for all contaminants present at the site for each discrete sampling event. Such maps allow interpretation of data on the distribution and the relative transport and degradation rates of contaminants in the subsurface. In addition, contaminant contour maps are necessary so that contaminant concentrations can be gridded and used for input into a numerical model. Detection of daughter products not present in the released NAPL (e.g., *cis*-1,2-DCE, VC, or ethene) provides evidence of reductive dechlorination. Preparation of contaminant isopleth maps is discussed in Appendix C.

If mobile and residual NAPLs are present at the site, a contour map showing the thickness and vertical and horizontal distribution of each should be prepared. These maps will allow interpretation of the distribution and the relative transport rate of NAPLs in the subsurface. In addition, these maps will aid in partitioning calculations and solute fate and transport model development. It is important to note that, because of the differences between the magnitude of capillary suction in the aquifer matrix and the different surface tension properties of NAPL and water, NAPL thickness observations made at monitoring points may not provide an accurate estimate of the actual volume of mobile and residual NAPL in the aquifer. To accurately determine the distribution of NAPLs, it is necessary to take continuous soil cores or, if confident that chlorinated solvents present as NAPL are commingled with fuels, to use cone penetrometer testing coupled with laser-induced fluorescence. Appendix C discusses the relationship between actual and apparent NAPL thickness.

2.4.1.6 Electron Acceptor, Metabolic By-product, and Alkalinity Contour Maps

Contour maps should be prepared for electron acceptors consumed (dissolved oxygen, nitrate, and sulfate) and metabolic by-products produced [iron (II), chloride, and methane] during biodegradation. In addition, a contour map should be prepared for alkalinity and ORP. The electron acceptor, metabolic by-product, alkalinity, and ORP contour maps provide evidence of the occurrence of biodegradation at a site. If hydrogen data are available, they also should be contoured.

During aerobic biodegradation, dissolved oxygen concentrations will decrease to levels below background concentrations. Similarly, during anaerobic degradation, the concentrations of nitrate and sulfate will be seen to decrease to levels below background. The electron acceptor contour maps allow interpretation of data on the distribution of the electron acceptors and the relative transport and degradation rates of contaminants in the subsurface. Thus, electron acceptor contour maps provide visual evidence of biodegradation and a visual indication of the relationship between the contaminant plume and the various electron acceptors.

Contour maps should be prepared for iron (II), chloride, and methane. During anaerobic degradation, the concentrations of these parameters will be seen to increase to levels above background. These maps allow interpretation of data on the distribution of metabolic by-products resulting from the microbial degradation of fuel hydrocarbons and the relative transport and degradation rates of contaminants in the subsurface. Thus, metabolic by-product contour maps provide visual evidence of biodegradation and a visual indication of the relationship between the contaminant plume and the various metabolic by-products.

A contour map should be prepared for total alkalinity (as CaCO_3). Respiration of dissolved oxygen, nitrate, iron (III), and sulfate tends to increase the total alkalinity of ground water. Thus, the total alkalinity inside the contaminant plume generally increases to levels above background. This map will allow visual interpretation of alkalinity data by showing the relationship between the contaminant plume and elevated alkalinity.

2.4.2 Pre-Modeling Calculations

Several calculations must be made prior to implementation of the solute fate and transport model. These calculations include sorption and retardation calculations, NAPL/water partitioning calculations, ground-water flow velocity calculations, and biodegradation rate-constant calculations. Each of these calculations is discussed in the following sections. The specifics of each calculation are presented in the appendices referenced below.

2.4.2.1 Analysis of Contaminant, Daughter Product, Electron Acceptor, Metabolic By-product, and Total Alkalinity Data

The extent and distribution (vertical and horizontal) of contamination, daughter product, and electron acceptor and metabolic by-product concentrations are of paramount importance in documenting the occurrence of biodegradation and in solute fate and transport model implementation.

Comparison of contaminant, electron acceptor, electron donor, and metabolic by-product distributions can help identify significant trends in site biodegradation. Dissolved oxygen concentrations below background in an area with organic contamination are indicative of aerobic biodegradation of organic carbon. Similarly, nitrate and sulfate concentrations below background in an area with contamination are indicative of anaerobic biodegradation of organic carbon. Likewise, elevated concentrations of the metabolic by-products iron (II), chloride, and methane in areas with contamination are indicative of biodegradation of organic carbon. In addition, elevated concentrations of total alkalinity (as CaCO_3) in areas with contamination are indicative of biodegradation of organic compounds via aerobic respiration, denitrification, iron (III) reduction, and sulfate reduction. If these trends can be documented, it is possible to quantify the relative importance of each biodegradation mechanism, as described in Appendices B and C. The contour maps described in Section 2.4.1 can be used to provide graphical evidence of these relationships.

Detection of daughter products not present in the released NAPL (e.g., *cis*-1,2-DCE, VC, or ethene) provides evidence of reductive dechlorination. The contour maps described in Section 2.4.1 in conjunction with NAPL analyses can be used to show that reductive dechlorination is occurring.

2.4.2.2 Sorption and Retardation Calculations

Contaminant sorption and retardation calculations should be made based on the TOC content of the aquifer matrix and the organic carbon partitioning coefficient (K_{oc}) for each contaminant. The average TOC concentration from the most transmissive zone in the aquifer should be used for retardation calculations. A sensitivity analysis should also be performed during modeling using a range of TOC concentrations, including the lowest TOC concentration measured at the site. Sorption and retardation calculations should be completed for all contaminants and any tracers. Sorption and retardation calculations are described in Appendix C.

2.4.2.3 NAPL/Water Partitioning Calculations

If NAPL remains at the site, partitioning calculations should be made to account for the partitioning from this phase into ground water. Several models for NAPL/water partitioning have been proposed in recent years, including those by Hunt *et al.* (1988), Bruce *et al.* (1991), Cline *et al.* (1991), and Johnson and Pankow (1992). Because the models presented by Cline *et al.* (1991) and Bruce *et al.* (1991) represent equilibrium partitioning, they are the most conservative models. Equilibrium partitioning is conservative because it predicts the maximum dissolved concentration when NAPL in contact with water is allowed to reach equilibrium. The results of these equilibrium partitioning calculations can be used in a solute fate and transport model to simulate a continuing source of contamination. The theory behind fuel/water partitioning calculations is presented in Appendix B, and example calculations are presented in Appendix C.

2.4.2.4 Ground-water Flow Velocity Calculations

The average linear ground-water flow velocity of the most transmissive aquifer zone containing contamination should be calculated to check the accuracy of the solute fate and transport model and to allow calculation of first-order biodegradation rate constants. An example of a ground-water flow velocity calculation is given in Appendix C.

2.4.2.5 Apparent Biodegradation Rate-Constant Calculations

Biodegradation rate constants are necessary to accurately simulate the fate and transport of contaminants dissolved in ground water. In many cases, biodegradation of contaminants can be approximated using first-order kinetics. In order to calculate first-order biodegradation rate constants, the apparent degradation rate must be normalized for the effects of dilution, sorption, and volatilization. Two methods for determining first-order rate constants are described in Appendix C. One method involves the use of a biologically recalcitrant compound found in the dissolved contaminant plume that can be used as a conservative tracer. The other method, proposed by Buscheck and Alcantar (1995) is based on the one-dimensional steady-state analytical solution to the advection-dispersion equation presented by Bear (1979). It is appropriate for plumes where contaminant concentrations are in dynamic equilibrium between plume formation at the source and plume attenuation downgradient. Because of the complexity of estimating biodegradation rates with these methods, the results are more accurately referred to as “apparent” biodegradation rate constants. Apparent degradation rates reflect the difference between contaminant degradation and production which is important for some daughter products (e.g., TCE, DCE, and VC).

2.5 SIMULATE NATURAL ATTENUATION USING SOLUTE FATE AND TRANSPORT MODELS

Simulating natural attenuation allows prediction of the migration and attenuation of the contaminant plume through time. Natural attenuation modeling is a tool that allows site-specific data to be used to predict the fate and transport of solutes under governing physical, chemical, and

biological processes. Hence, the results of the modeling effort are not in themselves sufficient proof that natural attenuation is occurring at a given site. The results of the modeling effort are only as good as the original data input into the model; therefore, an investment in thorough site characterization will improve the validity of the modeling results. In some cases, straightforward analytical models of solute transport are adequate to simulate natural attenuation.

Several well-documented and widely accepted solute fate and transport models are available for simulating the fate and transport of contaminants under the influence of advection, dispersion, sorption, and biodegradation.

2.6 CONDUCT A RECEPTOR EXPOSURE PATHWAYS ANALYSIS

After the rates of natural attenuation have been documented, and predictions from appropriate fate and transport models indicate that MNA is a viable remedy, the proponent of natural attenuation should combine all available data and information to provide support for this remedial option. Supporting the natural attenuation option generally will involve performing a receptor exposure pathways analysis. This analysis includes identifying potential human and ecological receptors and points of exposure under current and future land and ground-water use scenarios. The results of solute fate and transport modeling are central to the exposure pathways analysis. If conservative model input parameters are used, the solute fate and transport model should give conservative estimates of contaminant plume migration. From this information, the potential for impacts on human health and the environment from contamination present at the site can be assessed.

2.7 EVALUATE SUPPLEMENTAL SOURCE REMOVAL OPTIONS

Additional source removal, treatment, or containment measures, beyond those previously implemented, may be necessary for MNA to be a viable remedial option or to decrease the time needed for natural processes to attain site-specific remedial objectives. Several technologies suitable for source reduction or removal are listed on Figure 2.1. Other technologies may be used as dictated by site conditions and regulatory requirements. If a solute fate and transport model has been prepared for a site, the impact of source removal can readily be evaluated by modifying the contaminant source term; this will allow for a reevaluation of the exposure pathways analysis.

In some cases (particularly if the site is regulated under CERCLA), the removal, treatment, or containment of the source may be required to restore the aquifer as a source of drinking water, or to prevent discharge of contaminants to ecologically sensitive areas. If a solute fate and transport model has been prepared, it can also be used to forecast the benefits of source control by predicting the time required to restore the aquifer to drinking water quality, and the reduction in contaminant loadings to sensitive ecosystems.

2.8 PREPARE LONG-TERM MONITORING PLAN

This plan is used to monitor the plume over time and to verify that natural attenuation is occurring at rates sufficient to attain site-specific remediation objectives and within the time frame predicted at the time of remedy selection. In addition, the long-term monitoring plan should be designed to evaluate long-term behavior of the plume, verify that exposure to contaminants does not occur, verify that natural attenuation breakdown products do not pose additional risks, determine actual (rather than predicted) attenuation rates for refining predictions of remediation time frame, and to document when site-specific remediation objectives have been attained.

The long-term monitoring plan should be developed based on site characterization data, analysis of potential exposure pathways, and the results of solute fate and transport modeling. EPA is developing additional guidance on long-term monitoring of MNA remedies, which should be consulted when available.

The long-term monitoring plan includes two types of monitoring wells. Long-term monitoring wells are intended to determine if the behavior of the plume is changing. Performance evaluation wells are intended to confirm that contaminant concentrations meet regulatory acceptance levels, and to trigger an action to manage potential expansion of the plume. Figure 2.7 depicts a schematic that describes the various categories of wells in a comprehensive monitoring plan. Figure 2.7 is intended to depict categories of wells, and does not depict monitoring well placement at a real site. Included in the schematic representation are: 1) wells in the source area; 2) wells in unimpacted ground water; 3) wells downgradient of the source area in a zone of natural attenuation; 4) wells located downgradient from the plume where contaminant concentrations are below regulatory acceptance levels but geochemical indicators are altered and soluble electron acceptors are depleted with respect to unimpacted ground water; and 5) performance evaluation wells.

The final number and placement of long-term monitoring wells and performance evaluation wells will vary from site to site, based on the behavior of the plume as revealed during the site characterization and on the site-specific remediation objectives. In order to provide a valid monitoring system, all monitoring wells must be screened in the same hydrogeologic unit as the contaminant plume being monitored. This generally requires detailed stratigraphic correlation. To facilitate accurate stratigraphic correlation, detailed visual descriptions of all subsurface materials encountered during borehole drilling or cone penetrometer testing should be prepared prior to monitoring well installation.

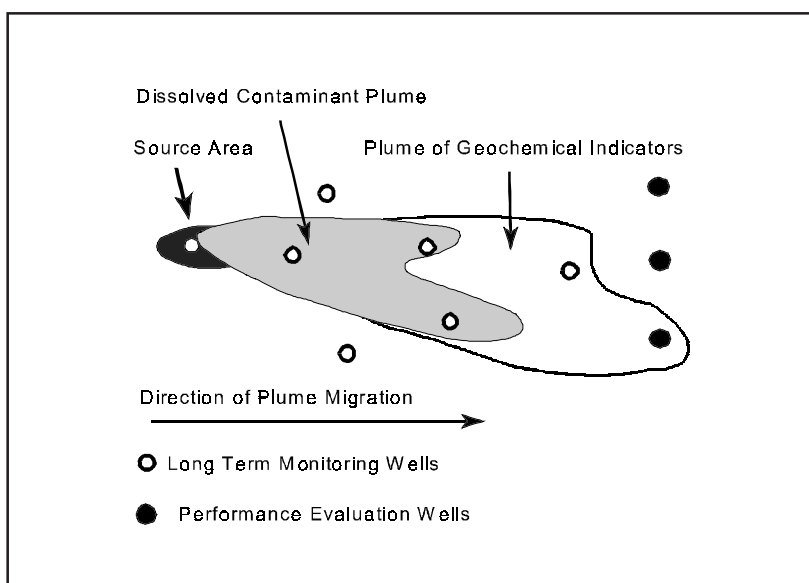


Figure 2.7 Hypothetical long-term monitoring strategy. Note that number and location of monitoring wells will vary with the three-dimensional complexity of the plume(s) and site-specific remediation objectives.

Although the final number and placement of long-term monitoring wells and performance evaluation wells should be determined through regulatory negotiation, the locations of long-term monitoring wells should be based on the behavior of the plume as revealed during the site characterization and on regulatory considerations. The final number and location of performance evaluation wells will also depend on regulatory considerations.

A ground-water sampling and analysis plan should be prepared in conjunction with a plan for placement of performance evaluation wells and long-term monitoring wells. For purposes of monitoring natural attenuation of chlorinated solvents, ground water from the long-term monitoring wells should be analyzed for the contaminants of concern, dissolved oxygen, nitrate, iron (II), sulfate, and methane. For performance evaluation wells, ground-water analyses should be limited to contaminants of concern. Any additional specific analytical requirements, such as sampling for contaminants that are metals, should be addressed in the sampling and analysis plan to ensure that all data required for regulatory decision making are collected. Water level and NAPL thickness measurements should be made during each sampling event.

Except at sites with very low hydraulic conductivity and gradients, quarterly sampling of both long-term monitoring wells and performance evaluation wells is recommended during the first year to help determine whether the plume is stable or migrating, the direction of plume migration and to establish a baseline for behavior of the plume. After the first year, an appropriate sampling frequency should be established which considers seasonal variations in water table elevations, ground-water flow direction and flow velocity at the site. If the hydraulic conductivity or hydraulic gradient are low, the time required for ground water to move from upgradient monitoring wells to downgradient monitoring wells should also be considered in determining the appropriate monitoring frequency. Monitoring of long-term performance of an MNA remedy should continue as long as contamination remains above required cleanup levels.

2.9 PRESENT FINDINGS

Results of natural attenuation studies should be presented in the remedy selection document appropriate for the site, such as CERCLA Feasibility Study or RCRA Corrective Measures Study. This will provide scientific documentation that allows an objective evaluation of whether MNA is the most appropriate remedial option for a given site.

All available site-specific data and information developed during the site characterization, conceptual model development, pre-modeling calculations, biodegradation rate calculation, ground-water modeling, model documentation, and long-term monitoring plan preparation phases of the natural attenuation investigation should be presented in a consistent and complementary manner in the feasibility study or similar document. Of particular interest to the site decision makers will be evidence that natural attenuation is occurring at rates sufficient to attain site-specific remediation objectives in a time period that is reasonable compared to other alternatives, and that human health and the environment will be protected over time. Since a weight-of-evidence argument will be presented to support an MNA remedy, all model assumptions should be conservative and all available evidence in support of MNA should be presented.